Effects of zircon on porous structure and alkali durability of borosilicate glasses

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Abstract

Additions of zircon ($ZrSiO_4$) were made to yield alkaline durable porous glasses based on the sodium borosilicate glass system. The glasses were characterised using differential thermal analysis (DTA) to identify the glass transition temperature and crystallisation temperature. The selected heat-treatment caused the glasses to phase separate by a spinodal decomposition mechanism. X-ray diffraction (XRD) was used to identify the crystalline phases. Acid leaching was used to remove the borate phase and create a porous structure. Scanning electron microscopy (SEM) revealed classic interconnected porous morphologies, while energy dispersive X-ray (EDX) analysis confirmed the presence of zirconium (Zr) in the porous silica-rich skeleton. Some of the porous glasses exhibited sharp and uniform pore distributions. Mean pore size ranged from 40 nm to 200 nm with a surface area from 5 to 35 m^2/g depending on glass composition and heat-treatment time. Zircon containing porous glasses are 3–4 times more alkali resistant than the parent sodium borosilicate glass.
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1. Introduction

Porous sodium borosilicate glass poses some unique properties, such as interconnected pore structure, chemical inertness, high mechanical and thermal stability, and high surface area, making it suitable for diversified use in the biological, electrical and pharmaceutical industries. It is known for its superior usability in membrane technology, size exclusion and affinity protein chromatography (separation science) [1–3]. For more than 30 yr, borosilicate glass has been used for the entrapment/immobilisation of high level waste from nuclear power plants and arms industries [4,5]. A low dielectric constant and negligible thermal expansion coefficient make it suitable for microelectronic packaging [6,7]. Moreover, the usage of borosilicate glass as a reinforced matrix component in composites to improve mechanical properties is widely accepted [8]. Increasing the chemical durability is one of the major challenges for porous borosilicate glass, to make it suitable and re-usable for many other applications. Borosilicate glass is known for its phase separation characteristics, thus enabling pore sizes of micro- meso- and macro-pore size, depending on the heating cycle [9].

The sodium borosilicate glass system is known to undergo amorphous phase separation (APS) by the spinodal decomposition mechanism [10]. Porous glass is derived from glass that is heat-treated to form two interconnecting phases: a silica-rich phase, and an alkali-rich borate phase. The heat-treated glass is then leached selectively to remove one of the phases. The heat-treatment step and leaching conditions can be adjusted to achieve the desired pore size, pore volume, and surface area. Therefore, porous glass based on the sodium borosilicate system can be tailor-made to required specifications with specific pore sizes over a wide range, thus offering flexibility in terms of end applications.

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As was stated earlier, porous silica glass with improved alkali-resistance has been the subject of many investigations. Up to 1 N NaOH is desirable for cleaning and sanitisation of chromatography columns used in the biopharmaceutical industry [11]. However, silica is attacked by alkali. This results in pore enlargement, leading to inaccurate separations and eventually to degradation of the silica support. Stout used a chemical precursor (containing zirconia) to impregnate the pores and coat the surface of glass to improve its durability [12]. There are a number of different types of precursor available, in the form of a solution containing ZrO_2 and organics. After coating, the organics are removed by heating to leave a layer of ZrO_2 bonded to the silica surface. This is a convenient method, since porous glass can be easily dipped in solution. Dipping under vacuum enables impregnation of pores, thereby providing a surface mosaic of zirconia and silicon oxide, which according to Jungbauer [11] can withstand short term use at pH 9.0. Murakami has also pursued a surface alteration approach [13], whereby porous glass is formed (by a traditional glass-making route) and then immersed in a solution of zirconium alcoholate to form a thin film of the zirconium salt, followed by hydrolysing, drying, calcining and formation of ZrO_2 polymer on the surface of the porous glass. Coating with zirconia in this way results in a slight decrease in pore diameter/pore volume, as the inner pore walls are coated. The alkali resistance is quoted as reduced percentage of sample when treated with zirconium tetra (n-butoxide) (1% aq. at 50 °C for 1 h), and for the material, this value was 7.3%, compared to 28.4% over the non-treated glass. Eguchi et al. continued the trend of using zirconia to improve the alkali durability of silica-based glass systems [14]. Rather than coating the glass surface however, the approach involved adding zirconia powder to the starting material composition. Wada et al. also made additions of zirconia to silicate glass, using sol–gel glasses [15]. McNeff et al. used spray drying as a technique to spray dry colloidal zirconia and generate zirconia microspheres [16]. The microspheres were modified with ethylenediamine-N,N-tetra (methylenephosphonic acid) (EDTPA) to create a cation-exchange chromatographic support. Porous metal oxides of 15–100 μm in average diameter with pore sizes ranging from 40 to 60 nm and surface areas from 10 to 50 m^2/g were prepared for the preparative purification of biomolecules.

Previously, these authors have attempted to increase the zirconia content in the porous glass by modifying the initial composition using a higher amount of alkali oxide (10 wt% of Na_2O) [17]. Although zirconia was found in the porous glass, the phase separation occurred by a nucleation and growth process and yielded low pore connectivity. Zircon ($ZrSiO_4$) could be a possible candidate to replace zirconia as it is more likely to affinitise with silica and remaining part of the glass skeleton formed during leaching. In this study, the thermal behaviour of sodium borosilicate glasses with addition of zircon was investigated, which to the best of our knowledge, has not been previously reported. A comparison was also made with zirconia-containing glass of similar composition. Heat-treatment

times and temperatures were optimised to achieve well-defined porous morphologies.

2. Experimental

2.1. Glass preparation

The compositions of glasses prepared in this study are detailed in Table 1. Compositions AA–EE involve substitution of SiO_2 with gradually increasing amounts of $ZrSiO_4$, keeping the content of Na_2O at 6 wt% and B_2O_3 at 25 wt%. Composition E-II was the same as EE, but with ZrO_2 replacing $ZrSiO_4$. SiO_2, B_2O_3, Na_2CO_3, ZrO_2 and $ZrSiO_4$ powders were procured from Sigma-Aldrich (Ireland). The glass reagents were ball-milled for 14 h. The mixed batches were melted in zirconia crucibles (Almath Ltd., UK) at 1450 °C for 2 h in an electric furnace. The melts were then water-quenched to produce frit. The glass frits were crushed in a ball mill for 12 h. The resultant powder was sieved to a particle size $> 45 \, \mu m < 212 \, \mu m$.

2.2. Thermal analysis

Differential thermal analysis (DTA) (Stanton Redcroft, UK) was used to measure the glass transition temperature (T_g) and to investigate the crystallisation behaviour. Heating rates of 10, 15, and 20 °C/min were employed using 30 mg of sample and alumina as a reference.

2.3. X-ray diffraction analysis (XRD)

Non heat-treated and heat-treated glass powders were analysed using XRD. A Bruker advanced D8 X-ray diffractometer with Ni-filtered Cu Kα radiation of wavelength 1.5406 Å at 40 kV and 40 mA was used to measure the XRD patterns with a step size of 0.1° in a range of 2θ values from 10 to 80° at scanning speed of 10 s/step. Crystalline phases present in heat-treated glass samples were identified by the positions listed in the joint commission on powder diffraction standards (JCPDS) files.

2.4. Heat treatment

Thermal treatment to induce phase separation was carried out on glass powder using a horizontal tube furnace (Carbolite Ltd., Sheffield, UK) at a heating rate of 10 °C/min. The dwell

Table 1
Composition of glasses in wt%.

Glass	SiO_2	B_2O_3	Na_2O	ZrO_2	$ZrSiO_4$
AA	69	25	6	0	0
CC	62	25	6	0	7
DD	58	25	6	0	11
EE	54	25	6	0	15
E-II	54	25	6	15	0